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CERTIFICATION

RWS SF Job No.: 86854
Lynch, Cox, Gilman & Mahan P.S.C.: P-1105
(Exothermal feeder mass)

I, KIMM ST. THOMAS, OF RWS GROUP, LLC, HEREBY CERTIFY THAT THE FOLLOWING IS, TO THE BEST OF OUR KNOWLEDGE AND BELIEF, A TRUE, COMPLETE AND ACCURATE GERMAN-LANGUAGE TRANSLATION OF THE ATTACHED GERMAN-LANGUAGE DOCUMENTS.

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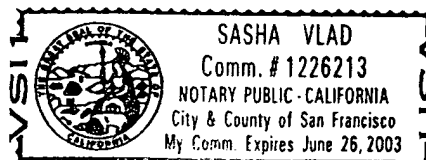
SAN FRANCISCO, CALIFORNIA

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November 21, 2001

Subscribed and sworn to before me this 21ST day of NOVEMBER, 2001

Sasha Vlad
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TRANSLATION FROM GERMAN

Patent Application

Exothermal feeder mass

Specification

The invention relates to an exothermal feeder mass containing aluminum and magnesium, at least one oxidizing agent, a temperature-resistant SiO_2 -containing filler, and an alkali silicate as the binder.

In exothermal feeder masses the aluminum is used to cause an exothermal reaction with the oxidizing agent, known feeder masses also containing a reactive fluorine compound which reacts with a passivating oxide skin on the aluminum powder so that the latter can react with the oxidizing agents.

One such feeder mass is described for example in DE-C-25 32 745. It contains among others aluminum powder, an unspecified aluminum oxide and an organic (phenol resin, urea resin or furan resin, starch) or an inorganic binder (silica sol, colloidal aluminum oxide) and an oxidizing agent for the fine-particle metal. The use of alkali silicates as binders is not mentioned. The fluorine compounds, called "fluoride catalysts", such as cryolite, fluorspar or sodium silicofluoride are important. The proportion of the fluorine compound can be 0.1 to 20% by weight; according to the examples the proportion of the fluoride compound is between 1.0 and 2.0%.

The presence of the fluorine compound in the exothermal feeder mass reduces the starting reaction temperature of the aluminum. This function results for example from the fact that for the likewise described heat-insulating feeder mass without aluminum the proportion of the fluoride compound can decrease to 0%.

DE-A-29 23 393 mentions among others exothermal feeder masses with aluminum powder, cryolite, iron oxide, sand and aluminum oxide fibers. The latter should be preserved as fibers.

DE-C-28 31 505 describes an exothermal feeder mass with an Al_2O_3 additive which however can be construed as an inert filler. Alkali silicates are not used, but the addition of a

fluoride-containing flux (cryolite) is always necessary. Magnesium is not used.

DD-60 121 describes an exothermal feeder mass based on aluminum with the addition of water glass and a fluoride- containing flux. Aluminum oxide is not mentioned.

Since for environmental and process-engineering reasons there is a need for a fluoride-free exothermal feeder mass, it has already been suggested that an exothermal feeder mass without active fluorine portions be made available. One such feeder mass contains not only aluminum, but also magnesium or an aluminum-magnesium alloy. The passivity caused by the oxide skin on the aluminum is overcome by the temperature which occurs when the magnesium burns so that the aluminum also reacts with the oxidizing agent, by which a higher temperature is reached overall. In doing so, unwanted reactions occur in the feeder mass.

It was found that for fluoride-free exothermal feeder masses which contain aluminum and magnesium and also fillers with high SiO_2 content and alkali compounds (for example, from water glass) as the binder and alkali nitrates as the oxidizing agent, a so-called "hollow fire" is formed which probably originates from vitrification of the SiO_2 -containing fillers with the alkali compounds.

The hollow fire is expressed in large cavities in the feeder wall which is connected by channels to the molten iron in the feeder. Iron losses occur due to penetration of the molten iron into the cavity. Moreover, this iron can only be separated from the reacted feeder mass with difficulty, so that it is almost impossible to re-generate the iron.

The object of this invention is to reduce the so-called "hollow fire".

It was found that surprisingly a hollow fire does not occur when a reactive or extremely finely ground aluminum oxide is added to the feeder mass.

The subject matter of the invention is thus an exothermal feeder mass of the initially mentioned type which contains roughly 2.5 to 20% by weight of a reactive aluminum oxide with a specific surface of at least roughly $0.5 \text{ m}^2/\text{g}$ and an average particle diameter (d_{50}) from roughly 0.5 to 15 microns and which is essentially free of fluoride-containing fluxes.

The reactive aluminum oxide generally contains up to roughly 5% OH groups. When the proportion of OH groups is relatively low, reactivity is also achieved by the very small size of the aluminum oxide particles.

"Essentially free" is defined as the fluoride content being below 1.0, preferably below 0.5, especially below 0.1% by weight.

The exothermal feeder mass as claimed in the invention after reaction shows only small cavities which are not connected to one another by channels so that no iron from the feeder core can penetrate.

The action of the reactive aluminum oxide can be imagined such that it reacts with the

existing alkali compounds so that they can no longer react with the SiO₂-containing filler with vitrification and cavity formation. When a hollow fire no longer occurs, during and after the end of the reaction of the feeder mass its strength also increases.

The reactive aluminum oxide in the feeder mass as claimed in the invention preferably has a specific surface of roughly 1 to 10 m²/g. Generally the composition of the feeder mass as claimed in the invention is as follows:

Aluminum: 20 - 35% by weight, preferably 20 - 23% by weight

Magnesium: 1.5 - 10% by weight, preferably 2 - 7% by weight

Oxidizing agent: 8 - 20% by weight, preferably 10 - 15% by weight

Reactive aluminum oxide: 4 - 18% by weight, preferably 8 - 13% by weight

Alkali silicate: 8 - 22% by weight, preferably 10 - 13% by weight or 17 - 23% by weight

SiO₂-containing filler: 58.5 - 17% by weight, preferably 43 - 29% by weight

The preferred amounts of the alkali silicate depend on the filler. For fillers with a smaller bulk density (for example, hollow microspheres) the preferred amount of the alkali silicate is higher.

The oxidizing agent, as in the known feeder masses, is iron oxide and/or an alkali nitrate, such as sodium or potassium nitrate, the reduction product of the latter (alkali nitrite or alkali oxide) reacting with the reactive aluminum oxide.

Preferably the SiO₂-containing filler has a SiO₂ content of at least 50% by weight, especially of more than 60% by weight.

The temperature-resistant SiO₂-containing fillers can be quartz sand and/or aluminum silicates, in the latter case preferably hollow microspheres, ground chamotte and/or mineral fibers being used.

The reactive aluminum oxide preferably has the following properties:

Al ₂ O ₃ content	> 90%
Content of OH-groups:	up to 5% (depending on the particle diameter)
Specific surface (BET)	roughly 1 to 10 m ² /g
Average particle diameter (d ₅₀):	0.5 to 15 microns

The subject matter of the invention is also a process for reducing the hollow fire in essentially fluoride-free feeder masses; the process is characterized by a feeder mass as defined above being used.

It was furthermore found that when using the feeder mass as claimed in the invention a change of the molten iron contained in the feeder, which change extends into the casting, surprisingly occurs. The basic metallic structure is changed such that degeneration of the solidified casting mass is prevented by the formation of flaky graphite and the desired spheroidal graphite is formed. This can possibly be attributed to the presence of magnesium in the feeder mass as a spherogenic additive, although it does not come directly into contact with the molten iron and therefore no interaction between the two could be expected. A reaction of the magnesium contained in the feeder mass with the molten iron in the vapor phase can be considered precluded, since magnesium has an extremely low vapor pressure and the feeder mass contains air inclusions between the grains of fine-grain mineral, so that the vaporous magnesium would immediately react with atmospheric oxygen. The effect which can be achieved by the invention is probably due to the fact that the feeder mass contains impurities (for example, sulfur) which can diffuse without the magnesium in the feeder mass into the molten iron and in this way can react with the very small amounts of the spherogenic additive (for example, magnesium) in the molten iron, so that when the iron solidifies, not spheroidal graphite, but flaky graphite, forms. It is assumed that the magnesium in the feeder mass reacts with the impurities contained therein so that they can no longer diffuse into the molten iron. The magnesium therefore apparently has a "scavenger" function.

In addition to the magnesium, also other spherogenic additives, such as cerium, can be used. Alkali metals or alkaline earth metals other than magnesium, for example, calcium, are not as well suited since they easily oxidize in air.

The subject matter of the invention is thus a process for preventing graphite degeneration in the feeder neck area and in the area which extends into the casting; this process is characterized by a feeder mass as defined above being used.

The invention is explained by the following examples.

Example 1

Formulation:

Aluminum (0.063 - 0.5 mm grain size)	20% by weight
Sodium nitrate as oxidizing agent:	15% by weight
Magnesium (0.1 - 0.5 mm grain size)	4.5% by weight
Reactive Al ₂ O ₃ : Al ₂ O ₃ content 99%, BET surface < 6 m ² /g, d ₅₀ 4-8 microns	9% by weight
SiO ₂ sand (0.1 - 0.5 mm grain size)	40.5% by weight
Water glass (43 - 45% solution)	11% by weight

The components are thoroughly mixed, and a feeder mold is filled with the resulting mass. The feeder mold is gassed with carbon dioxide; the water glass reacts with the carbon dioxide with the formation of colloidal silicic acid and sodium carbonate and hardens the feeder. Then the mass is dried until the weight is constant.

The feeder is placed on the casting pattern and thus rammed up, whereupon molten iron is poured into the mold. In doing so the feeder mass ignites as the temperature rises, the sodium carbonate obtained from the water glass and the reaction product of the sodium nitrate preferably reacting with the reactive Al₂O₃ so that the hollow fire which occurs during the reaction with sand is reduced. After the end of the casting process the feeder is removed. After the reaction the feeder shows in cross section a host of small cavities which are not interconnected by channels and thus which do not contain any iron either (Figure 1).

Example 2

Formulation:

Aluminum (as in example 1)	20% by weight
Sodium nitrate (as in example 1)	10% by weight
Magnesium (as in example 1)	4% by weight
Reactive Al ₂ O ₃ (as in example 1)	12.5% by weight
SiO ₂ hollow microspheres (0 - 0.5 mm grain size) bulk weight 350 cm ³ /g, SiO ₂ content 55-65%)	36.5% by weight

Water glass (as in example 1)

17% by weight

The components are mixed with one another as in example 1, placed in a feeder mold, gassed with carbon dioxide, and dried. Casting is also carried out as in example 1. The cross section of the reacted feeder mass shows essentially the same pore structure as the feeder from example 1.

Example 3 (comparison)

The formulation was the same as in example 1, but instead of reactive Al_2O_3 , 9% by weight Al_2O_3 with the following properties were used: Al_2O_3 content 99%, grain size 0 to 0.5 mm ($d_{50} = 200$ microns).

Processing continued as in example 1. The resulting feeder (see Figure 2 for an extract from the feeder wall) after the reaction shows a major hollow fire with a large cavity volume in the center which is connected via channels to smaller cavities which extend into the region of the molten iron. All the cavities are filled with solidified iron. When the feeder is crushed, residues of the reacted feeder mass adhere to the pieces of iron. The compressive strength of the conventionally produced cylindrical test piece ($d = 50$ mm, $h = 50$ mm) for quality control of the feeder mass from Example 3 is roughly 35% less than that of the test piece from Example 1.

Claims

1. Exothermal feeder mass, containing aluminum and magnesium, at least one oxidizing agent, a SiO₂-containing filler, and an alkali silicate as the binder, characterized in that it contains roughly 2.5 to 20% by weight of a reactive aluminum oxide with a specific surface of at least roughly 0.5 m²/g and an average particle diameter (d₅₀) from roughly 0.5 to 8 microns and that it is essentially free of fluoride-containing fluxes.

2. Feeder mass as claimed in claim 1, wherein the reactive aluminum oxide has a specific surface of roughly 1 to 10 m²/g.

3. Feeder mass as claimed in claim 1 or 2, characterized by the following composition:

- aluminum: 20 - 35% by weight, preferably 22 - 28% by weight
- magnesium: 1.5 - 10% by weight, preferably 2 - 7% by weight
- oxidizing agent 8 - 20% by weight, preferably 10 - 15% by weight
- reactive aluminum oxide 4 - 18% by weight, preferably 8 - 13% by weight
- alkali silicate: 8 - 22% by weight, preferably 10 - 13% by weight or 17 - 22% by weight
- temperature-resistant SiO₂-containing filler: 58.5 - 17% by weight, preferably 43 - 29% by weight

4. Feeder mass as claimed in one of claims 1 to 3, wherein the oxidizing agent is iron oxide or an alkali nitrate.

5. Feeder mass as claimed in one of claims 1 to 4, wherein the temperature-resistant SiO₂-containing filler has a SiO₂ content of at least 50% by weight, especially of more than 60% by weight.

6. Feeder mass as claimed in one of claims 1 to 5, wherein the temperature-resistant SiO₂-containing fillers are quartz sand and/or aluminum silicates.

7. Feeder mass as claimed in claim 6, wherein the temperature-resistant SiO₂-containing fillers are hollow microspheres, ground chamotte and/or mineral fibers.

8. Feeder mass as claimed in one of claims 1 to 6, wherein the reactive aluminum oxide has the following properties:

Al₂O₃ content > 90%

Content of OH-groups: up to 5%
Specific surface (BET): 1 to 10 m²/g

Average particle diameter (d₅₀): 0.5 to 15 microns

9. Process for reducing the hollow fire in essentially fluoride-free feeder masses, wherein a feeder mass as claimed in one of claims 1 to 8 is used.

10. Process for preventing graphite degenerations in the feeder neck area and in the area which extends into the casting, wherein a feeder mass as claimed in one of claims 1 to 8 is used.

Abstract

An exothermal feeder mass is described, containing aluminum and magnesium, at least one oxidizing agent, a SiO₂-containing filler, and an alkali silicate as the binder; it is characterized in that it contains roughly 2.5 to 20% by weight of a reactive aluminum oxide with a specific surface of at least roughly 0.5 m²/g and an average particle diameter (d₅₀) from roughly 0.5 to 8 microns and is essentially free of fluoride-containing fluxes.